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The first commercial vacuum roll coater designed specifically for ITO sputter deposition was built by Leybold in 1983 and installed at Sierracin Corp. in 1984. This coater had three coating stations and three dc planar magnetrons. It was capable of coating substrates up to 1524 mm wide and could process rolls of film 533 mm in diameter on 152 mm cores.

DTI started to develop an ITO sputter deposition process in 1980. By 1983 they were producing significant amounts of sputter deposited ITO from a roll coater (1575 mm) that was built and designed in house [5]. This coater had 3 dc planar magnetron cathodes and used a free span web path configuration. One of their products was a two side coated 3 mm thick polycarbonate film used as a transparent anti static window for microchip tote boxes. Ben Meckel of DTI gave a paper in 1984 at the 27th annual SVC TechCon describing their work on ITO sputter deposition [5].

Several Japanese companies also developed ITO roll coating capabilities by the early 1980's. Teijin patented a process to first deposit InSn by sputtering or evaporation on to PET film substrates and then post oxidizing the coating [3,6]. This method produces very dense, hard and highly crystalline ITO layers. The post annealing process also effectively heat stabilized the PET film. Toray installed a Leybold sputter roll coater in 1981 and was producing ITO coated PET films within a year. In 1985 Leybold sold 3 more sputter roll coaters designed to produce ITO coated polymer films to Sumitomo Bakelite, Daicel and Gunze [7].

In the 28<sup>th</sup> annual SVC TechCon, I.V. Runyan of Coulter presented a paper describing their unique RF sputter deposition roll coater [30]. This coater, designed and built by Leybold, had 12 RF sputter cathodes and could coat films as wide as 910 mm. They used the coater primarily to deposit CdS onto stainless steel foils. However Mr. Runyan did show samples of ITO on PET films made by RF sputtering at the conference. The RF coating process proved to be too costly and hard to control and work on making ITO was soon abandoned.

In 1986 a detailed paper describing the basic physical properties of sputtered deposited ITO using vacuum roll coaters was presented by M. Mayr of Leybold at the 29th annual SVC TechCon [8]. He also discussed the problems of large scale manufacturing of ITO roll coatings, the basic design of an ITO sputter roll coater and the properties of a typical ITO coating sputter deposited onto PET films.

J. Matteucci of Flex Products presented a paper at the 30<sup>th</sup> SVC TechCon discussing their ITO roll coating capability [9]. He described a 65 ohm/sq. ITO coating on PET that was 120 nm thick and had a visible light transmission (VLT) of 80%. They had also developed an anti reflected version of this film which had a 90% VLT.

W. H. Brady installed a production roll coater in 1988 and completed a development effort to produce patterned ITO on a continuous web of PET film [10]. This process was sold to Dynapro in 1993. The patterned ITO/PET is used mainly for the in house manufacturing of transparent touch screens.

By 1991 the manufacturers of ceramic ITO targets had made significant strides in improving their products. These improvements were mainly driven by the liquid crystal display manufacturers who required a very high quality ITO coating on glass substrates. Several roll coating companies began to use these improved ceramic targets in their equipment. Courtaulds Performance Films (CPF) presented a detailed study comparing the quality and deposition rates of ITO films made by direct and reactive sputtering techniques at the 34<sup>th</sup> annual SVC TechCon [11].

In 1990 Leybold introduced the concept of the medium frequency ac magnetron for use in reactive sputter deposition of oxides and nitrides. This approach proved to be very useful for these processes because it solved the "vanishing anode problem" [12]. A paper comparing the properties of transparent conductive oxides, including ITO, deposited by dc and pulsed dc was presented by the Fraunhofer Institute for Surface Engineering and Thin Films and Leybold Systems at the 5<sup>th</sup> International Plasma Surface Engineering Conference [13]. The first roll coater using Leybold's ac magnetrons, called TwinMAG<sup>TM</sup>, was installed in Japan in 1994 [7]. This coater also has Leybold's SpeedMag<sup>TM</sup> magnetrons. These cathodes use a specially designed magnetic field with arc suppression circuitry to improve target utilization and sputtering rate [12]. It is believed, but not confirmed, that this coater is capable of making ITO films.

The concept of rotatable cathodes was introduced to vacuum roll coating in 1988 [14]. These cathodes offer far better target utilization rates and allow for a higher power density for faster sputtering rates. The first vacuum roll coater that used rotatable cathodes and is capable of depositing ITO was delivered to DTI in 1992. Ceramic ITO rotatable targets were introduced in 1997 by I. S. T. [15].

## TECHNOLOGY FOR ITO ROLL COATING

ITO roll coating is a subset of a more generalized technology, the deposition of transparent conductive (TC) thin films for various applications. In an excellent review paper by T.C. Chopra, et. al. (16) the authors point out that "ever since the first report of transparent conducting CdO films prepared by the thermal oxidation of sputtered Cd by Badeker (17) in 1907, the technological interest in transparent conductors has grown tremendously."

The technology discussed in this section is specific to ITO and even more specific to coating a heat sensitive polymeric

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substrate in the form of a web. While the technology for sputter roll coating ITO is relatively new (as can be seen from the first section of this paper), the science of creating free electrons by introducing non stoichiometry in a wide band gap oxide has been well understood for decades. This is done in indium oxide by substituting tin for indium in an indium oxide matrix. In each case free (conduction) electrons are generated, resulting in conductivity. A more detailed discussion of this is given by M. Mayr in a presentation given at the SVC TechCon in 1986 (8).

Conductivity of the ITO is further influenced by coating defects that scatter the conduction electrons. Such defects are grain boundaries, inclusions or structural disorders resulting from the coating conditions. In general defect free, high density and smooth films of ITO result in the highest conductivities. Unfortunately the energy (or temperature) limitations of the polymeric substrates used in ITO roll coating limit the amount of energy input that can be used to minimize the defect density in the coating.

Therefore, the objective of the technology of sputter roll coating of ITO is to create a dense high temperature coating on a low temperature substrate. In spite of these limitations specific resistivities as low as  $1.7 \times 10^{-4}$  ohm-cm on polymeric substrates have been reported (18). However, most reported values for commercially available ITO products with  $R_s$  values in the range of 60 to 100 ohm/sq. are 6 to  $8 \times 10^{-4}$  ohm-cm.

The deposition of ITO is now a fairly standard vacuum coating technology. A wide variety of companies offer various types of equipment and control system for the manufacturing of ITO. Direct dc sputtering of ITO from a partially oxidized ITO ceramic target results in high quality, low defect coatings with the least difficulty in process control. By regulating the level of oxygen partial pressure in the sputtering chamber the optical absorption and conductivity can be controlled. Thickness of the deposited layer is selected for the optimum optical thickness ( $n \times d$ , where  $n$  is the index of refraction of the layer and  $d$  is the thickness) to meet application specific values. Typically some type of in vacuum optical monitor is used to assure meeting the optical specifications while an in vacuum monitor for measuring the  $R_s$  is used to achieve control of the sheet resistivity.

Reactive dc sputtering of ITO from an alloy metal target requires far more complex control systems as evidenced by the many papers published on the subject. In a recent article by Patel et. al. (19) the reactive technology is reviewed and several useful references are cited. In essence the transition mode process is stabilized either by a tight control loop using feedback from plasma and gas conditions or by using an open control loop with very high gas flows to stabilize the process. While high gas flow methods are very effective, they

require high throughput pumping systems.

Reactive medium frequency (MF) sputtering of ITO is emerging not so much driven by ITO but by the need to deposit dielectrics that make highly insulating layers that are troubled by the "disappearing anode" effect (20) when deposited using dc reactive technology. There are strong indications that an enhancement of film properties can be realized using MF sputtering from a twin cathode configuration (13) due likely to an increase in the energy per adatom ratio in the depositing film. This is consistent with our objective to deposit high temperature structures on low temperature substrates. However, this effect has to be balanced against the damage to the growing ITO layer that such bombardment might cause.

Rotatable magnetrons are used effectively to deposit ITO from ceramic targets (20, 14) but the target fabrication must be recognized as a key element in realizing the full economic advantage of this technology (15). Typically they are operated in the direct dc mode with anodes designed to prevent the "disappearing anode" effect.

Deposition methods and conditions predispose the material for arrival at the substrate but the surface that receives the coating always influences the properties of the layer. The energetic deposit creates a micro environment at the surface that can cause fusing, outgassing and chemical mixing with the arriving ITO coating. In almost all web coaters the substrate is wrapped tightly on a drum but heat transfer is limited by the gaseous medium between web and drum (21). Great attention to this issue is critical to the coating quality. Preparation of the substrate by a glow discharge step is typically practiced and built into the sputter coater. Specific treatments are closely guarded by most producers of ITO products. However there is an excellent review on the effect of reactive gas plasma treatment on materials (22) and another article that discusses the properties of commercial polymer films following plasma treatment (23).

There are only two types of targets in general use for depositing ITO. They are the InSn alloy and the ceramic. Alloys are prepared by casting the low melting material into a mold or directly into a grooved backing plate. Because the target can be easily refreshed by simply adding more material, the economics favor the alloy targets. But in cooling some segregation occurs that creates regions that are not completely homogeneous. This results in short range compositional gradients in the target. Voids resulting from the shrinkage pipes that occur on solidification are usually healed by surface heating to remelt them. By mechanically working the material one can homogenize the material, but the economic advantage of casting is then lost.

Ceramic targets are made by a variety of methods including hot isostatic pressing (HIP), cold isostatic pressing (CIP),

slip casting and hot pressing. In every case the density of the target needs to be as high as possible. But another important factor is the method of target attachment to the backing plate and the power limitation placed upon the target by the bonding. Some cathode constructions place water directly on the back of the backing plate: others have an indirect cooling method. Manufacturers will specify the maximum power density capability for their designs

A limitation of sputtering from a ceramic target, and to some degree from a metal one as well, is formation of cones in or adjacent to the erosion groove that ultimately limit the sputter rate by covering the target and acting as arc initiators. Two papers on cones are cited here (24), (25) that present a comprehensive treatment of the subject. Additional work needs to be done and reported upon before a recipe for control of coning can be claimed.

In summary, it is impossible in a brief treatment of such a complex technology as ITO roll coating to address all the issues, so the reader is referred to the references cited in this paper. There are also many other excellent papers that support the conclusions presented in this section, especially those found in past issues of the SVC Technical Conference proceedings.

#### **CURRENT MARKETS FOR ITO ROLL COATING**

In 1997 the worldwide production volume for ITO coatings on continuous rolls of polymeric substrates is estimated to be between 15 to 17 million square feet. This market has been growing at an annual rate of over 10% for the last 5 years and is expected to continue to grow at this same rate for the next three to five years. Currently North America supplies approximately 60% of the total ITO roll coated film sold while the Far East produces over 35%. Almost all of this 35% is done in Japan. There is very little ITO coating activity in Europe or the rest of the world. It is anticipated that within the next several years the Far East will produce at least 50% of the roll coated ITO made. Once again, most of this will come from Japan, although companies in Korea, Taiwan and China are expressing interest in this technology.

The majority of ITO roll coating is done on PET optical grade film bases. Most of the PET films coated are 75, 100, 125 and 175 microns thick, with the last two gauges being the most popular. However, the latest trend appears to favor the use of thinner gauge films for cost savings. Heat stabilized and abrasion resistant hard coated PET films are frequently required by the end user.

ITO coated PET (ITO/PET) films are normally provided with  $R_s$  in the range of 60 ohms/ $\square$  to 400 ohms/ $\square$ . The VLT values are usually specified as  $> 80\%$ . Coatings with  $R_s$  values greater than 500 ohms/ $\square$  tend to be unstable due to the thinness of the ITO layer. There have been some ITO coatings

deposited on polymeric substrates with  $R_s$  values down to 20 ohms/ $\square$ . However, these coatings are quite thick (between 250 and 300 nm.) and therefore very expensive to make. Moreover, they have a distinct yellowish cast to them due to the absorption in the blue of the ITO coating and tend to be quite brittle, making them susceptible to cracking and difficult to handle.

The most common uses for roll coating ITO products are as transparent electrodes. Thick film electroluminescent (EL) lamps use about 45% of the roll coated ITO on PET. The major applications for these lamps are as backlights and in signage. The range of  $R_s$  used for EL lamps is between 200-400 ohms/ $\square$ . Heat stabilized PET is used in EL lamps because of the need to cure the phosphor containing slurry used in their manufacture. Growth in the use of ITO/PET for EL lamps appears to be slowing down in the near term.

Transparent membrane switches and touch panels use close to 35% of the ITO/PET annual production. Applications in this area include digitizing pads for pen input devices, shopping mall kiosks, product locators for shoppers and instrumentation control panels. Long term growth in this area is expected to be strong, passing EL lamps in the next couple of years. The range of  $R_s$  used for these applications is 60 to 400 ohms/sq., depending on the switch design. Abrasion resistant coated PET film is required in most applications. Other end uses for ITO transparent electrodes include smart windows, transparent heating elements and RFI/EMI shielding.

The other major use for roll coated ITO is in transparent and anti static shielding. It can be used by itself or in combination with other layers such as part of an anti reflective stack. The anti static/anti reflective application has been commercialized during the last two years and is predicted to grow rapidly in the future. This growth is being driven by the need to anti reflect display devices in a cost effective manner.

Other film substrates coated with ITO are polyimide (PI), polyethylene naphthalate (PEN), cellulose triacetate (CTA), polyether sulfone (PES) and polycarbonate (PC). ITO coated PI films are used in the construction of thermal control satellite blankets. The ITO acts as an anti static layer to prevent the build up of electrical charge carried by the solar winds. ITO/CTA is used as an anti static layer in some display related applications. ITO coated PES and PC films are starting to be used in flexible film based liquid crystal displays being manufactured by Ricoh and Teijin respectively. This LCD application is expected to grow rapidly over the next few years. Substrates used in most LCD designs must not be optically birefringent, since they are used in conjunction with polarizers. This is why PET is not usually considered as useful substrate for LCD applications. PEN has a higher glass transition temperature than PET and is therefore a candidate for use in processes that require this.

The major North American manufacturers of sputter roll coated ITO films, listed by their estimated annual production volumes in 1997, are Courtaulds Performance Films, Dynapro Thin Film Products, Southwall Technologies, MSC Specialty Films, Techni-Met and VDI. The first three companies in the list probably produced close to 80% of the ITO roll coated film made in North America. However, almost all of Dynapro's production is consumed internally for the manufacture of touch panels.

In the Japanese market place, Nitto Denko and Oike are the largest manufacturers of roll coated ITO, each with about 30% of the market. Gunze is the third largest producer of these coatings but uses most of its volume internally for making touch panels. Sumitomo Bakelite and Toray also produce ITO roll coating products. For reference, a detailed description of the Japanese market situation was presented at the 1989 SVC TechCon (26).

### FUTURE TRENDS FOR ITO ROLL COATING

ITO will probably remain the dominant transparent conductive coating for at least the next 3-5 years. Other candidate materials do not seem to possess the same combination of performance, environmental stability and cost that ITO does (27, 28, and 29). Sputter deposition roll coating will continue to be the preferred coating process, because it is a well characterized technology and relatively easy to control. It is unclear whether the use of ac magnetrons will replace the standard dc magnetrons in reactive ITO processes. This is because of the high level of bombardment of energetic species that is associated with this process on the depositing ITO layer. However, the uses of pulsed dc magnetrons and SpeedMag™ cathodes, both of which incorporate effective designs for reducing arcs, should continue to increase in the future. There is not enough data available yet to determine if rotatable cathodes will have any significant impact in the production of ITO roll coated products.

The markets that will continue to drive the growth of sputter roll coated ITO films will be touch panels and flat panel displays. For touch panels, the growing popularity of the hand held personal data assistants (PDA) and computers will fuel this growth. Improvements in transmittance, environmental performance and mechanical durability are being requested by the end users. Cost reduction is also considered important. Flat panel display manufacturers are looking for ways to reduce the cost of their displays and to make them more rugged. This is especially true for the lower information content displays used in such applications as cellular telephones, electronic games, automobile dashboards and home appliances. The use of roll coated ITO on polymer substrates is a way of accomplishing both goals. However, there are some technical issues to overcome, such as the need for a high water vapor barrier, higher conductivity ITO coatings and protection of the polymer substrate from chemical attack by

liquid crystals, before there will be wide spread use of ITO roll coatings in flat panel displays.

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